

# PATENT SPECIFICATION



704,231

Date of filing Complete Specification Oct. 20, 1949.

Application Date Nov. 12, 1948.

No. 29481/48.

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Index at acceptance :--Classes 2(4), D(1T : 2) ; and 15(2), B2(A2 : E).

## PROVISIONAL SPECIFICATION

SPECIFICATION NO. 704,231

By a direction given under Section 17(1) of the Patents Act 1949 this application proceeded in the name of Farbenfabriken Bayer Aktiengesellschaft, a German Body Corporate, of Leverkusen-Bayerwerk, Germany.

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THE PATENT OFFICE,  
1st December, 1954

DB 70627/1 (27) /3493 150 11/54 R

15 aine for dyeing from the vat. These indications refer both to unsulphonated and sulphonated products, specific mention being made of the copper, nickel and iron complexes. In reality, unsulphonated 20 copper and nickel phthalocyanines have no vatting properties. Sulphonation products thereof are capable of being vatted but do not dye the fibre from the vat to any material extent. Unsulphonated as 25 well as sulphonated iron phthalocyanines are capable of use as vat dyes, also exhibit some affinity to the fibre, but yield unsatisfactory shades.  
It has now been found that cobalt 30 phthalocyanines are far superior to all other phthalocyanines as far as vatting properties are concerned. Contrary to the unsubstituted copper and nickel complexes the unsubstituted cobalt phthalocyanine is capable of use as a vat dye and, 35 on dyeing from the vat, yields essentially clearer shades than the iron complex. The property of vatting and yielding clear valuable dyes, on textiles from the vat 40 is not restricted to the unsubstituted cobalt phthalocyanine. According to the present invention, the above properties to a larger extent are met with those substitution products of cobalt phthalocyanine the hydrophilic property of which has been increased by substitution. For accomplishing this, i.e., substituents of different kinds may be used, for instance, sulphinic acid groups, sulphonamide 45 groups (the nitrogen of which may be 50 sulphophthalic acid, e.g., 4-methoxyphthalic acid, 4-nitro phthalic acid, or other hydrophilic substituted *o*-dicarboxylic acids or the functional derivatives thereof. As a matter of fact, besides such substituents as increase the hydrophilic property, the 55 cobalt phthalocyanines may also contain substituents which exert the contrary effect, provided however, that there are sufficient hydrophilic substituents in order to accomplish at least a higher 60 hydrophilic character than in the case of unsubstituted cobalt phthalocyanine. All 65 these substitution products have generally better vatting properties than the unsubstituted cobalt phthalocyanine itself. This 70 is true with the reservation that the number of hydrophilic groups must not be so high as to render the products easily soluble in water as otherwise the affinity 75 for the fibre of the vatted product will be 80 impaired.

The present invention also comprises the application of cobalt phthalocyanines with increased hydrophilic properties in admixture with the unsubstituted cobalt 85 phthalocyanine or with cobalt phthalocyanines containing other substituents. It has been found that even small amounts of hydrophilic cobalt phthalocyanines will do to convert larger amounts of non-hydrophilic cobalt phthalocyanines with poor vatting properties into a state in which they exhibit excellent vatting properties. Such mixtures may be obtained in a simple manner, for instance, by start- 90 95 100

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Price 2s. 6d.

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## PROVISIONAL SPECIFICATION

### Improvements in and relating to Vat Dyestuffs

We, FARBENFABRIKEN BAYER, a German Company, of 22c, Leverkusen-Bayerwerk, Germany, do hereby declare the nature of this invention to be as follows:—

5 The present invention relates to the use of certain phthalocyanines as vat dyestuffs.

The phthalocyanines which are distinguished by clear shades and excellent fastness properties have been used for pigmenting, as substantive dyestuffs and as dyestuffs for lake-making. In British Specification No. 322,169 some indications are given of phthalocyanines being suitable for dyeing from the vat. These indications refer both to unsulphonated and sulphonated products, specific mention being made of the copper, nickel and iron complexes. In reality, unsulphonated as

20 copper and nickel phthalocyanines have no vatting properties. Sulphonation products thereof are capable of being vatted but do not dye the fibre from the vat to any material extent. Unsulphonated as

25 well as sulphonated iron phthalocyanines are capable of use as vat dyes, also exhibit some affinity to the fibre, but yield unsatisfactory shades.

It has now been found that cobalt 30 phthalocyanines are far superior to all other phthalocyanines as far as vatting properties are concerned. Contrary to the unsubstituted copper and nickel complexes the unsubstituted cobalt phthalocyanine is capable of use as a vat dye and, on dyeing from the vat, yields essentially

35 clearer shades than the iron complex. The property of vatting and yielding clear valuable dyeings on textiles from the vat

40 is not restricted to the unsubstituted cobalt phthalocyanine. According to the present invention, the above properties to a larger extent are met with those substitution products of cobalt phthalocyanine the hydro-

45 philic property of which has been increased by substitution. For accomplishing this effect, substituents of different kinds may be used, for instance, sulphonic acid groups, sulphonamide groups (the nitrogen of which may be

mono- or disubstituted by alkylaryl- or aralkyl radicals), sulphonic acid groups, carboxylic acid groups, carboxylic amide groups, cyano groups, hydroxy groups, alkoxy groups, mercapto groups, alkyl- 55 mercapto groups, nitro groups, amino groups, or acylamino groups. These

groups may be introduced into the cobalt phthalocyanine as usual, i.e. either subsequently to complex formation or in the course of preparing the complex by starting from phthalic acids, phthalonitriles or other phthalocyanine starting materials containing such substituents, e.g. 4-

45 sulphophthalic acid, 4-methoxyphthalic acid, 4-nitro phthalic acid, or other hydrophilic substituted o-dicarboxylic acids or the functional derivatives thereof. As a matter of fact, besides such substituents

50 as increase the hydrophilic property, the cobalt phthalocyanines may also contain substituents which exert the contrary effect, provided however, that there are sufficient hydrophilic substituents in order to accomplish at least a higher 70.

55 hydrophilic character than in the case of unsubstituted cobalt phthalocyanine. All these substitution products have generally better vatting properties than the unsub-

60 substituted cobalt phthalocyanine itself. This 80 is true with the reservation that the number of hydrophilic groups must not be so high as to render the products easily soluble in water as otherwise the affinity

65 for the fibre of the vatted product will be 85 impaired.

The present invention also comprises the application of cobalt phthalocyanines with increased hydrophilic properties in admixture with the unsubstituted cobalt 90 phthalocyanine or with cobalt phthalocyanines containing other substituents.

It has been found that even small amounts of hydrophilic cobalt phthalocyanines will do to convert larger amounts of non- 95 hydrophilic cobalt phthalocyanines with poor vatting properties into a state in which they exhibit excellent vatting properties. Such mixtures may be obtained in a simple manner, for instance, by start- 100

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ing the cobalt phthalocyanine synthesis from a preponderant amount of phthalic acid in admixture with a small amount of hydrophilic substituted phthalic acids.

5 Another possibility of preparing such dyestuff mixtures consists in subsequently introducing small amounts of hydrophilic substituents into the phthalocyanine molecule, e.g. by sulphonation.

10 Among the various combinations of cobalt phthalocyanines with hydrophilic groups and such without hydrophilic groups as described in the foregoing paragraph, mixtures of the unsubstituted

15 cobalt phthalocyanine with low sulphonated cobalt phthalocyanines are of the greatest importance. In the preparation of such cobalt phthalocyanine sulphonnic acids care must be taken that, as

20 far as possible, only monosulphonic acids will be obtained. Such mixtures may be prepared either by cautiously sulphonating cobalt phthalocyanine or by starting the phthalocyanine synthesis from a mix-

25 ture of smaller amounts of sulphophthalic acid with larger amounts of phthalic acid. Mixtures thus obtained may be blended with unsulphonated cobalt phthalocyanine so as to exhibit the desired degree of solu-

30 bility. The best results are obtained from combinations of sulphonated cobalt phthalocyanine and unsulphonated cobalt phthalocyanine in which the cobalt phthalocyanine sulphonnic acids are pre-  
35 sent in an amount of 15—40% by weight (calculated as monosulphonic acid).

In these mixtures, sulphonnic acid groups can be replaced with a similar effect by alkylamino groups.

40 Cobalt phthalocyanine and the various hydrophilic substitution products mentioned above as well as the combinations described in the foregoing will dye cellulose fibres according to the methods

45 usually applied to vat dyestuffs. In general, the best affinity is reached when dyeing from the hot vat. Many cobalt phthalocyanines are capable of being vatted even in a weakly alkaline medium,

50 for instance, in the presence of ammonia and, therefore, may also be used for dyeing animal fibres from the vat.

The following examples illustrate the 55 invention without being restricted thereto, the parts and percentages being by weight.

Examples A—C describe various dyeing processes whereas Examples 1—22 refer to 60 the preparation of various dyestuffs to be used for such dyeing processes.

#### EXAMPLE A.

Describes the vat dyeing with cobalt phthalocyanine vat dyestuffs on cotton:—

100 parts of a cobalt phthalocyanine 55 paste (corresponding to 1 part of the 100% dyestuff) are added to 650 parts of water and 9.5 parts of concentrated caustic soda solution (38° Bé) of 50° C. 44 parts of sodium hydrosulphite solution (1:10 dis-  
70 solved in water) are caused to react with the above mixture for 15 minutes at 50° C. 208 parts of Glauber's salt solution (1:10 dissolved in water) are then added and 50 parts of cotton are dyed in the usual 75 manner at 50° C. for one hour. After lifting the cotton is squeezed off and hung in the air for 10 minutes; it is rinsed in cold water, the dyeing is treated with dilute sulphuric acid (3.7 parts per 1000 80 parts of water) and it is rinsed once more with water. The dyeing is then washed at the boil with Marseilles soap (2 parts per 1000 parts of water), rinsed and dried. Full, blue to green, olive-green or grey 85 shades are obtained.

#### EXAMPLE B.

4.1 parts of caustic soda solution of 38° Bé, 20 parts of a paste of a cobalt phthalocyanine 1:100 (corresponding to 90 0.2 part) and 8.8 parts of a sodium hydrosulphite solution (1 part dissolved per 10 parts of water) are added to 170 parts of water of 60° C. After 15 minutes 10 parts of cotton are dyed therein in the usual 95 manner and, after hanging in the air, it is aftertreated as described in Example A. This process can be modified by increasing the quantity of caustic soda solution by 6.15 parts and by adding 42 parts of 100 Glauber's salt solution (1 part per 10 parts of water).

#### EXAMPLE C.

Describes the process of a vat dyeing on wool:—

105 0.2 part of a cobalt phthalocyanine capable of being easily vatted (for instance the dyestuff obtained according to Example 22) is vatted by means of 1.8 parts of concentrated ammonia (25%) and 110 0.75 part of sodium hydrosulphite in 120 parts of water at about 75° C. The vat is then filled up to 500 parts by adding water. 10 parts of wool are dyed in this liquor in the usual manner at 51—52° C. 115 for 1 hour. After lifting and wringing out the wool is hung in the air for 20 minutes, rinsed with water and treated with dilute acetic acid (5.5 parts of glacial acetic acid per 1000 parts of water), rinsed 120 and dried. Dyeings of good fastness properties are obtained.

#### EXAMPLE 1.

Describes the preparation of a mixture 125 capable of being easily vatted of a cobalt phthalocyanine sulphonnic acid with cobalt phthalocyanine:—

with good vatting properties from cobalt phthalocyanine and phosgene:—

10 parts of cobalt phthalocyanine are added at 120—130° C. to 100 parts of a mixture of aluminium chloride and sodium chloride (7:1). Phosgene is introduced at 150—155° C. As soon as a sample of the mix is capable of being readily vatted but not yet soluble in dilute caustic soda solution or only slightly soluble, the reaction is stopped and the dyestuff is isolated as usual. The dyestuff may either be used directly for vat dyeing or, after drying and pasting from sulphuric acid, in the presence of the same amount of cobalt phthalocyanine. In the latter case, somewhat redder and fuller shades are obtained.

#### EXAMPLE 7.

20 A mixture of:—  
 5.55 parts of phthalic acid anhydride  
 0.53 „ of trimellitic acid  
 1.87 „ of cobalt sulphate (83%)  
 1.177 „ of ammonium chloride  
 25 14.5 „ of urea, and  
 0.17 part of ammonium molybdate is gradually added to 16.8 parts of nitrobenzene of 180° C. The melt is further heated at 180° C. for 6 hours while stirring. The dyestuff is recovered and purified as described in Example 2. The dyestuff thus obtained dyes cotton from an olive-coloured vat full, clear, blue shades of good fastness to water and excellent fastness to light.

#### EXAMPLE 8.

Describes the preparation of a dyestuff with good vatting properties from cobalt phthalocyanine and phthalic anhydride.

40 A mixture of:—  
 1 part of cobalt phthalocyanine  
 2 „ of anhydrous aluminium chloride, and  
 10 „ of phthalic anhydride

45 is heated up to 210° C. for about 45 minutes until the reaction product exhibits good vatting properties.

The working up of the mixture can be performed either in an acid or in an alkaline medium. The dyestuff dyes cotton from the vat full, greenish-blue shades.

#### EXAMPLE 9.

A mixture of:—  
 55 8.5 parts of 4-bromophthalic anhydride  
 3.05 „ of phthalimide - 4 - sulphonamidemethylamide  
 2.35 „ of cobalt sulphate (83%)  
 1.25 „ of ammonium chloride  
 60 12.00 „ of urea, and  
 0.2 part of ammonium molybdate is gradually added while stirring to 22 parts of trichlorobenzene of 180° C. and

the melt is further heated at 180° C. for about 6 hours.

On proceeding as described in Example 2 a cobalt phthalocyanine is obtained which after pasting dyes cotton from an olive-coloured vat full, greenish shades.

#### EXAMPLE 10.

On proceeding according to Example 3, replacing, however, 2.26 parts of phthalimide-4-sulphamide by an equivalent amount of 4-nitrophthalic acid there is obtained a dyestuff which dyes cotton from the vat full, greenish-blue shades of good fastness to water and very good fastness to light.

#### EXAMPLE 11.

A mixture of:—  
 16.9 parts of 4-nitrophthalic acid  
 3.1 „ of cobalt sulphate (83%)  
 2.35 „ of ammonium chloride  
 29.0 „ of urea, and

0.35 part of ammonium molybdate is gradually added while stirring to 42.5 parts of trichlorobenzene at 180° C. and the melt is further heated at 180° C. for 6—7 hours.

On proceeding as described in Example 2 there is obtained 4.4<sup>1</sup>.4<sup>n</sup>.4<sup>111</sup>-tetranitrocobalt phthalocyanine in a good yield which dyes cotton from a yellow-coloured vat very full-olive-green shades, the nitro groups being converted thereby into amino groups. The dyeings which are distinguished by very good fastness to light can be diazotized on the fibre and can be reacted in the usual way with coupling components, very full, olive-green to dark green dyeings of very good fastness to light and excellent fastness to water being obtained thereby.

#### EXAMPLE 12.

A mixture of:—  
 6.00 parts of 4-acetylaminophthalic acid  
 1.26 „ of cobalt sulphate (83%)  
 0.78 „ of ammonium chloride  
 9.8 „ of urea, and  
 0.11 part of ammonium molybdate is gradually added while stirring to 21.6 parts of nitrobenzene at 180° C. and the melt is further heated while stirring at 180° C. for 6 hours. On proceeding as described in Example 2 a cobalt phthalocyanine is obtained which, after pasting, dyes cotton from an olive-green coloured vat bluish-green shades of excellent fastness to light.

#### EXAMPLE 13.

A mixture of:—  
 7.36 parts of 4-methoxyphthalic acid  
 1.87 „ of cobalt sulphate (83%)  
 1.17 „ of ammonium chloride  
 0.17 part of ammonium molybdate and  
 14.5 parts of urea

- 1.6 parts of cobalt phthalocyanine are gradually added while stirring into 20 parts of 10% fuming sulphuric acid at room temperature. The green solution thus obtained is heated for about 4 hours at 35–38° C. until a sample which has been washed neutral with water begins to dissolve on heating with pyridine water. This degree of sulphonation is reached when about 2.7–2.9% of sulphur have entered the molecule of the cobalt phthalocyanine. When this point is reached sulphonation is stopped and the solution is diluted below 40° C. with 36 parts of sulphuric acid of 66° Bé. When the solution shows only a small amount of free SO<sub>2</sub>, 2.4 parts of cobalt phthalocyanine are added below 25° C. and, as soon as dissolution is completed, the whole is stirred into about 400 parts of ice water. The precipitated dyestuff is filtered off and washed with hot water. The product dyes cotton from an olive coloured vat full, clear greenish-blue shades which are distinguished by excellent fastness to light.
- A vat dyestuff of equal dyeing properties is obtained by heating 20 parts of cobalt phthalocyanine in 150 parts of 10% fuming sulphuric acid at 45–48° C. for 2–3 hours until a sample which has been washed neutral with water can easily be vatted with sodium hydrosulphite and dilute caustic soda solution. If this is not the case, further 10–20 parts of 20% fuming sulphuric acid have to be added. The dyestuff is precipitated by stirring the solution into ice water and washing the precipitate with hot water.
- EXAMPLE 2.**
- 40 Describes the preparation of a cobalt phthalocyanine with good vatting properties from phthalic acid anhydride and sodium 4-sulphophthalate.
- A mixture of:—
- 45 10.36 parts of phthalic acid anhydride  
2.86 „ of sodium 4-sulphophthalate  
3.74 „ of cobalt sulphate (83%)  
2.34 „ of ammonium chloride  
50 29.00 „ of urea and  
0.34 „ of ammonium molybdate  
is gradually added to 24 parts of nitrobenzene at 180° C. and the melt is further heated at 180° C. for about 6 hours. About 60 parts of volume of methanol are stirred into the melt white hot. The dyestuff thus obtained is filtered off by suction and washed with methanol. By boiling with dilute hydrochloric acid, filtering off by suction and washing with water the impurities are removed from the dyestuff. After drying about 19.8 parts of a cobalt phthalocyanine are obtained which, after redissolving from sulphuric acid mono-
- hydrate, dyes cotton from an olive coloured vat full, clear, blue shades of excellent fastness to light.
- EXAMPLE 3.**
- A mixture of:—
- |                                       |    |
|---------------------------------------|----|
| 4.44 parts of phthalic acid anhydride | 70 |
| 2.26 „ of phthalimide-4-sulphamide    |    |
| 1.55 „ of cobalt sulphate (83%)       |    |
| 1.18 „ of ammonium chloride           |    |
| 14.5 „ of urea and                    | 75 |
| 0.18 part of ammonium molybdate       |    |
- is gradually added to 21.2 parts of trichlorobenzene and the melt is further heated at 180° C. for 5–6 hours. On proceeding as described in Example 2 a cobalt phthalocyanine with good vatting properties is obtained which dyes cotton full, very clear, blue shades of excellent fastness to light. The colour of the vat is olive.
- EXAMPLE 4.**
- A mixture of:—
- |  |    |
|--|----|
| 11.1 parts of phthalic acid anhydride        |    |
| 6.1 „ of phthalimide - 4 - sulphomethylamide | 90 |
| 4.7 „ of cobalt sulphate (83%)               |    |
| 2.5 „ of ammonium chloride                   |    |
| 24.0 „ of urea, and                          |    |
| 0.4 part of ammonium molybdate               |    |
- is gradually added to 44 parts of trichlorobenzene of 180° C. and the melt is further heated at 180° C. for about 6 hours. On proceeding as described in Example 2 a cobalt phthalocyanine is obtained which after pasting from a mixture of sulphuric acid monohydrate and chlorosulphonic acid (5:1), dyes cotton from a yellow-olive coloured vat full, blue shades of good fastness to water and excellent fastness to light.
- EXAMPLE 5**
- A mixture of:—
- |   |     |
|---|-----|
| 8.88 parts of phthalic acid anhydride         |     |
| 5.08 „ of phthalic acid-4-sulphodimethylamide | 110 |
| 3.74 „ of cobalt sulphate (83%)               |     |
| 2.34 „ of ammonium chloride                   |     |
| 29.00 „ of urea, and                          |     |
| 0.34 part of ammonium molybdate               |     |
- is gradually added to 24 parts of nitrobenzene of 180° C. and the melt is further heated at 180° C. for about 6 hours.
- On proceeding as described in Example 2 a cobalt phthalocyanine is obtained which, after pasting from a mixture of sulphuric acid monohydrate and chlorosulphonic acid (5:1), dyes cotton from a yellow-olive coloured vat full, greenish-blue shades of excellent fastness to light and good fastness to water.
- EXAMPLE 6.**
- Describes the preparation of a dyestuff

is gradually added while stirring to 22 parts of trichlorobenzene at 180° C. Thereupon, the dyestuff is recovered and purified as described in Example 2.

5      4.4<sup>1</sup>.4<sup>11</sup>.4<sup>111</sup>-tetramethoxy cobalt phthalocyanine thus obtained dyes cotton from a yellow-olive coloured vat full, clear turquoise blue shades of excellent fastness to light and very good fastness to water.

#### EXAMPLE 14.

10     Describes the preparation of a dyestuff with good vatting properties from cobalt phthalocyanine and sulphur chloride.

Starting at 50° C., 4 parts of cobalt 15 phthalocyanine are added to a mixture of 12 parts of anhydrous aluminium chloride and 24 parts of sulphur chloride, the temperature being raised thereby to 60° C. The temperature is kept at 60° C. until a 20 sample treated with sodium hydrosulphite and dilute caustic soda solution yields a clear, olive-brown vat, this stage being achieved after about 3 hours. The greenish-blue, vat dyestuff can be separated, 25 for instance, by introducing the reaction mixture into dilute hydrochloric acid. The dyestuff is filtered off by suction and washed with water.

For further purification the paste of the 30 crude dyestuff is extracted with sodium sulphide solution, a small amount of a greenish-blue dyestuff being dissolved thereby besides sulphur. The insoluble blue dyestuff is filtered off, washed with 35 water and dried, and can be used directly for dyeing from the vat.

#### EXAMPLE 15.

A mixture of:—

40     13.32 parts of phthalic anhydride  
6.33    "    of 4-nitrophthalic acid  
5.6      "    of cobalt sulphate (83%)  
3.51    "    of ammonium chloride  
43.5    "    of urea, and  
0.51 part of ammonium molybdate  
45 is added while stirring to 52.5 parts of nitrobenzene at 180° C. and the whole is further heated while stirring at 180° C. for 5—6 hours. On proceeding as described in Example 2, 4-mononitro cobalt phthalocyanine is obtained which, in the usual way, is converted on reduction with sodium sulphide into 4-monoamino cobalt phthalocyanine and, at last, into 4-monomercapto cobalt phthalocyanine by diazotizing and treating the diazonium compound with potassium thiocyanate and saponifying. 4 - monomercapto cobalt phthalocyanine dyes cotton from a yellow-olive coloured vat full, green to blue 60 shades of excellent fastness to light.

#### EXAMPLE 16.

On proceeding according to Example 15 starting, however, from 8.88 parts of

phthalic anhydride and 12.66 parts of 4-nitrophthalic acid, 4.4<sup>1</sup>-dimercapto cobalt 65 phthalocyanine is obtained which dyes cotton from the vat full, blue to green shades.

#### EXAMPLE 17.

On proceeding according to Example 15 70 starting, however, from 4.44 parts of phthalic anhydride and 18.99 parts of 4-nitrophthalic acid, 4.4<sup>1</sup>.4<sup>11</sup>-trimercapto cobalt phthalocyanine is obtained which dyes cotton from a yellow-olive coloured 75 vat bright, full, bluish-green shades of excellent fastness to light.

#### EXAMPLE 18.

On proceeding according to Example 15 leaving out, however, phthalic anhydride 80 and using 25.32 parts of 4-nitrophthalic acid, 4.4<sup>1</sup>.4<sup>11</sup>.4<sup>111</sup>-tetranitrocobalt phthalocyanine is obtained. 4.4<sup>1</sup>.4<sup>11</sup>.4<sup>111</sup>-tetra-mercaptopacobalt phthalocyanine obtainable therefrom dyes cotton from an olive 85 coloured vat greyish-green shades which, on after-treating with bichromate in acetic acid, turn fully grey, the fastness to water being very good.

#### EXAMPLE 19.

90

A mixture of:—

4.84 parts of diphenyl-3.4-dicarboxylic acid	
4.80    "    of phthalimide-4-sulpho-	
methylamide	95
1.84    "    of cobalt sulphate (83%)	
0.98 part of ammonium chloride	
9.44 parts of urea, and	
0.16 part of ammonium molybdate	

is introduced while stirring into 17.6 parts 100 of trichlorobenzene at 180° C. and the dyestuff is recovered and purified as described in Example 2. The cobalt dyestuff thus obtained dyes, after pasting from ethyl sulphuric acid, cotton from a 105 yellow-olive coloured vat full, greenish-blue shades.

#### EXAMPLE 20.

A mixture of:—

3.68 parts of 4-methoxyphthalic acid	110
4.84    "    of diphenyl - 3.4 - dicar-	
boxylic acid	
1.87    "    of cobalt sulphate (83%)	
1.17    "    of ammonium chloride	
14.5    "    of urea, and	115

0.17 part of ammonium molybdate  
is introduced while stirring into 22 parts of trichlorobenzene at 180° C. and the melt is further heated while stirring at 180° C. for 5—6 hours. On proceeding as 120 described in Example 2 a cobalt phthalocyanine is obtained which, after pasting from ethyl sulphuric acid, dyes cotton from a yellow-olive coloured vat clear, full, greenish-blue shades of good fastness 125 to water and excellent fastness to light.

	EXAMPLE 21.	A mixture of:—	30
	A mixture of:—		
	43.0 parts of benzophenone	22 parts of urea	
5	4.53 .. of anthraquinone-2 <sup>11</sup> -carbonyl - 4 <sup>1</sup> - amino - 3.4-di-cyanodiphenyl (prepared from 4 <sup>1</sup> - amino - 3.4 - di-cyanodiphenyl and anthraquinone-2-carboxylic acid chloride)	18 .. of condensation product of 4-aminophthalimide and the chloride of trimethyl-amino acetic chloride	35
10	3.84 .. of phthalodinitrile, and 1.62 .. of dehydrated cobalt chloride	2.8 .. of cobalt sulphate (83%)	
15	is heated after adding a small amount of pyridine at 240—245° C. for about 3—4 hours. After cooling down to about 80—90° C. the melt is diluted with 84 parts of methanol and the separated dyestuff is filtered off by suction. By washing with methanol, boiling with dilute hydrochloric acid and boiling with <i>o</i> -dichlorobenzene the dyestuff is obtained in a pure state. The dyestuff dyes cotton from a yellow-brown coloured vat clear blue-green shades of good fastness to water.	1.8 .. of ammonium chloride	
20		0.25 part of ammonium molybdate and 2.2 parts of benzamide	
25		is introduced at 180° C. into a stirring vessel and the melt is stirred at 180—185° C. for 2—3 hours. The melt being still in a warm condition is diluted with 440 parts of water, acidified with hydrochloric acid and the dyestuff thus obtained is salted out by adding 1060 parts of common salt solution. The dyestuff can be purified by dissolving once more in dilute hydrochloric acid and salting out with common salt and is soluble in dilute mineral acids with a bluish-green colour.	40 45

Dated this 12th day of November, 1948.

CARPMAELS & RANSFORD,  
Agents for Applicants,  
24, Southampton Buildings,  
London, W.C.2.

#### COMPLETE SPECIFICATION

#### Improvements in and relating to the use of Vat Dyestuffs

We, FARBFENFABRIKEN BAYER, a German Company, of 22c, Leverkusen-Bayerwerk, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

60 The present invention relates to the use of certain phthalocyanines as vat dyestuffs.

The phthalocyanines which are distinguished by clear shades and excellent fastness properties have been used for pigmenting, as substantive dyestuffs and as dyestuffs for lake-making. In British Specification No. 322,169 some indications are given of phthalocyanines being suitable for dyeing from the vat.

These indications refer both to unsulphonated and sulphonated products, specific mention being made of the copper nickel and iron complexes. In reality, unsulphonated copper and nickel phthalocyanines have no vatting properties. Sulphonation products thereof are capable of being vatted but do not dye the fibre from the vat to any material extent. Unsulphonated as well as sulphonated iron phthalocyanines are capable of use as vat dyes, also exhibit some affinity to the fibre, but yield unsatisfactory shades.

It has now been found that cobalt

phthalocyanines are far superior to all other phthalocyanines as far as vatting properties are concerned. Contrary to the unsubstituted copper and nickel complexes the unsubstituted cobalt phthalocyanine, preferably in the presence of auxiliary agents, for instance, pyridine, or (di)-hydroxyethylthioether, is capable of use as a vat dye and, on dyeing from the vat yields essentially clearer shades than the iron complex. The property of vatting and yielding clear valuable dyeings on textiles from the vat is not restricted to the unsubstituted cobalt phthalocyanines. According to the present invention, the above properties to a larger extent are met with in those substitution products of cobalt phthalocyanine the hydrophilic property of which has been increased by substitution. For accomplishing this effect, substituents of different kinds may be used, for instance, sulphonic acid groups, sulphonamide groups (the nitrogen of which may be mono- or disubstituted by alkyl-, aryl- or aralkyl radicals), sulphonic acid groups, carboxylic acid groups, carboxylic amide groups, cyano groups, hydroxy groups, alkoxy groups, mercapto groups, alkylmercapto groups, nitro groups, amino groups, alkylamino groups or acylamino groups. The production of some of these substituted cobalt

phthalocyanine dyestuffs is described and claimed in co-pending Application No. 13341/52 (Serial No. 704,310). All these substitution products have generally better vatting properties than the unsubstituted cobalt phthalocyanine itself. This is true with the reservation that the number of hydrophilic groups must not be so high as to render the products easily soluble in water as otherwise the affinity for the fibre of the vatted product will be impaired.

The present invention also comprises the application of cobalt phthalocyanines with increased hydrophilic properties in admixture with the unsubstituted cobalt phthalocyanine or with cobalt phthalocyanines containing other substituents. It has been found that even small amounts of hydrophilic cobalt phthalocyanines will do to convert larger amounts of non-hydrophilic cobalt phthalocyanines with poor vatting properties into a state in which they exhibit excellent vatting properties.

Among the various combinations of cobalt phthalocyanines with hydrophilic groups and such without hydrophilic groups as described in the foregoing paragraph, mixtures of the unsubstituted cobalt phthalocyanine with low sulphonated cobalt phthalocyanines are of the greatest importance. The preparation of such cobalt phthalocyanine sulphonic acids is described in co-pending Application No. 13341/52 (Serial No. 704,310). The best results are obtained from combinations of sulphonated cobalt phthalocyanine and unsulphonated cobalt phthalocyanine in which the cobalt phthalocyanine sulphonic acids are present in an amount of 15—40% by weight (calculated as monosulphonic acid).

In these mixtures, sulphonic acid groups can be replaced with a similar effect by alkylamino groups.

Cobalt phthalocyanine and the various hydrophilic substitution products mentioned above as well as the combinations described in the foregoing will dye cellulose fibres according to the methods usually applied to vat dyestuffs. In general, the best affinity is reached when dyeing from the hot vat. Many cobalt phthalocyanines are capable of being vatted even in a weakly alkaline medium, for instance, in the presence of ammonia and, therefore, may also be used for dyeing animal fibres from the vat.

The following examples illustrate the invention without being restricted thereto, the parts and percentages being by weight.

The cobalt phthalocyanine dyestuffs referred to in these examples may be

obtained according to Examples 1—5, 7, 10—13, 15—18 and 22 of the accompanying provisional specification.

#### EXAMPLE A.

Describes the vat dyeing with cobalt phthalocyanine vat dyestuffs on cotton:

100 parts of a paste of a cobalt phthalocyanine dye stuff (corresponding to 1 part of the 100% dyestuff) are added to 650 parts of water and 9.5 parts of concentrated caustic soda solution (38° Be) of 50° C. 44 parts of sodium hydrosulphite solution (1:10 dissolved in water) are caused to react with the above mixture for 15 minutes at 50° C. 208 parts of Glauber's salt solution (1:10 dissolved in water) are then added and 50 parts of cotton are dyed in the usual manner at 50° C. for one hour. After lifting the cotton is squeezed off and hung in the air for 10 minutes; it is rinsed in cold water, the dyeing is treated with dilute sulphuric acid (3.7 parts per 1000 parts of water) and it is rinsed once more with water. The dyeing is then washed at the boil with Mar-90 seilles soap (2 parts per 1000 parts of water), rinsed and dried. Full, blue to green, olive-green or grey shades are obtained.

#### EXAMPLE B.

4.1 parts of caustic soda solution of 38° Be, 20 parts of a paste of a cobalt phthalocyanine 1:100 (corresponding to 0.2 part) and 8.8 parts of a sodium hydrosulphite solution (1 part dissolved per 10 parts of water) are added to 170 parts of water of 60° C. After 15 minutes 10 parts of cotton are dyed therein in the usual manner and, after hanging in the air, it is after treated as described in Example A. 105 This process can be modified by increasing the quantity of caustic soda solution to 6.15 parts and by adding 42 parts of Glauber's salt solution (1 part per 10 parts of water). 110

#### EXAMPLE C.

Describes the process of a vat dying on wool.

0.2 part of a cobalt phthalocyanine capable of being easily vatted (for instance the dyestuff obtained according to Example 22 of the accompanying provisional specification) is vatted by means of 1.8 parts of concentrated ammonia (25%) and 0.75 part of sodium hydrosulphite in 120 120 parts of water at about 75° C. The vat is then filled up to 500 parts by adding water. 10 parts of wool are dyed in this liquor in the usual manner at 51—52° C. for 1 hour. After lifting and wringing 125 out the wool is hung in the air for 20 minutes, rinsed with water and treated with dilute acetic acid (5.25 parts of glacial acetic acid per 1000 parts of

water), rinsed and dried. Dyeings of good fasteness properties are obtained.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the manufacture and production of vat dyeings which consists in treating the material to be dyed in an alkaline vat with a vat dyestuff comprising cobalt phthalocyanine or its sulphonlic acid, sulphonamide, sulphonic acid, carboxylic acid, carboxylic amide, cyano, hydroxy, alkoxy, mercapto, alkylmercapto, nitro, amino, alkylamino and acylamino substitution products, water and a water-soluble reducing agent.
2. A process, as claimed in claim 1 in which the vat dyestuff comprises a mixture of a hydrophilic substituted cobalt phthalocyanine and cobalt phthalocyanine or a non-hydrophilic substituted cobalt phthalocyanine.

3. A process for the manufacture and production of vat dyeings which consists in treating the material to be dyed in an alkaline vat with a vat dyestuff comprising a mixture of cobalt phthalocyanine sulphonlic acids with substituted or unsubstituted cobalt phthalocyanines containing about from 15 to 40 per cent by weight of cobalt phthalocyanine sulphonlic acids calculated as monosulphonlic acid, water and a water-soluble reducing agent.

4. The process for the manufacture and production of vat dyeings substantially as described in the Examples A—C.

5. Materials dyed in the vat when obtained according to the process as claimed in claims 1—4.

Dated this 20th day of October, 1949.

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